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The Polarity and Strength of the Intermolecular Hydrogen Bond

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The results of studies on the dipole moments and the thermodynamics of the formation of complexes with an intermolecular hydrogen bond are reviewed and the nature of the relation between the energies and lengths of intermolecular hydrogen bonds is examined. The enthalpy-entropy relations for the formation of hydrogen-bonded complexes and the linear correlation between the energy of charge transfer and the hydrogen bond energy are analysed and validated. The theoretical and experimental results of the study of hydrogen-bonded complexes are examined from the standpoint of the donor-acceptor nature of hydrogen bonds.
The bibliography includes 240 references.

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I. INTRODUCTION

Numerous studies have been made on hydrogen bonds. The interest in this common type of coordination interaction can be accounted for by its exceptionally important role in many physical, chemical, and biological processes. A number of books[1-6], general reviews[7,8], as well as reviews on specific aspects of the hydrogen bond (theory[9-16], infrared and ultraviolet spectroscopy[17,18], NMR[19-25], and reactivity[26]) have been written. There exists an appreciable gap in the survey of results of studies on the polar properties of hydrogen bonds and in this field there exists only a short and extremely limited review[27].

Nevertheless the dipole moment is one of the most important characteristics of the molecular complex, since it carries information about the nature of the redistribution of electron density and complex formation. This parameter assumes particular importance when hydrogen-bonded complexes are examined from the standpoint of the donor–acceptor interaction, since it makes it possible to assess the role of charge-transfer forces in the stabilisation of hydrogen-bonded complexes.

In the present review, an attempt is made to survey the results of studies on the polar properties of intermolecular hydrogen-bonds, to examine the question of the type of correlation between the polarity and energy of hydrogen bonds, and to discover the common features and differences in the properties of hydrogen-bonded complexes and the usual complexes of the donor–acceptor type (EDA complexes). Mainly studies concerned with hydrogen-bonded complexes formed by neutral molecules A–H and B are dealt with in the review. Furthermore, the results which make it possible to determine fairly reliably the parameters characterising intermolecular hydrogen bonds are given preferential consideration.

It is usual to refer to the components of the (A–H)–B system as acid–base, or proton donor–proton acceptor, or electron acceptor–electron donor respectively. In the main, we shall use the terminology electron donor (B) and electron acceptor (A–H).

II. THE NATURE OF THE HYDROGEN BOND

The theoretical aspect of the hydrogen bond has been examined in detail in the monographs and reviews mentioned above and will not be discussed here. We shall only point out that a characteristic feature of research in this field is a consistent increase in the number and sophistication of studies devoted to both semi-empirical and, particularly, non-empirical (*ab initio*) quantum-mechanical calculations on systems with hydrogen bonds. The latter is to a large extent due to the development of methods for calculations on multielectron systems and to the improvement of computational techniques.

The results of calculations of electron density redistribution and molecular orbital populations on formation of hydrogen bonds are the most important from the standpoint of the understanding of the nature of the hydrogen bond. Despite the wide variety of systems for which calculations have been made, general trends can be recognised[10-12]. When a hydrogen bond is formed, electron density shifts from the donor molecule B to the acceptor molecule A–H. This type of electron density redistribution has been observed also on formation of the usual donor–acceptor bond[28]. This factor justifies the consideration of hydrogen-bonded complexes as complexes of the donor–acceptor type. The magnitude of the transferred charge differs in different systems. For example, it amounts to only 0.0064*e* for the water dimer[29] and to 0.04*e* and 0.07*e* for the more stable complexes[30] $HOH.NH_3$ and $FOH.NH_3$. Here the decrease of electron density at the electron donor atom causes a charge redistribution in the entire molecule B. The greatest increase of electron density is observed in the region of the atom X of the electron acceptor molecule A–X–H.[31-36]

In the solution of the problem of intermolecular interaction, the question of the forces leading to the formation of complexes is extremely important. There have been numerous studies designed to obtain quantitative estimates of the contributions of Coulombic attraction, exchange repulsion, inductive and dispersion interactions, and the

stabilisation energy of relatively weak hydrogen bonds[9,11]. Using perturbation theory, Murrell and coworkers[37,38] developed a method which can take into account not only the electrostatic interactions but also the effects of the overlapping of the interacting orbitals of the donor and acceptor molecules. This procedure makes it possible to trace the trend in the changes of individual contributions with increasing strength of the interaction. It has been shown that the role of the inductive and exchange system energies is not great: the main contribution to the energy of hydrogen bonds comes from the Coulombic interaction. The charge-transfer energy is low when the overlap integral S of the interacting orbitals is less than 0.1, but increases rapidly with increase of S.[38] Consequently the contribution of the charge-transfer energy is low for weak hydrogen bonds, becoming more important for moderately strong and strong hydrogen bonds. This hypothesis is consistent with the results from the analysis of the contribution of different forces to the stabilisation energy of the usual complexes of the donor–acceptor type.

The contributions of the polarisation interaction to the dipole moment (μ_c, D) and to the energy of formation (ΔH, kcal mole^{-1}) of a number of charge-transfer complexes are given below:

Complex	μ_c	$-\Delta H$ (calc.)	μ_c	$-\Delta H$ (expt.)
HMB*-chloranil (Ref.39)	0.5—0.9	2.2—2.4	1.0	5.4
HMB*-trinitrobenzene (Ref.39)	1.1—1.5	2.6—3.0	0.87	4.7
$I_2.NH_3$ (Ref.40)	0.91—1.96	0.34—1.68	6.4	4.8
$I_2.N(CH_3)_3$ (Ref.40)	0.30—0.57	0.04—0.13	6.0	10.2

† Hexamethylbenzene.

Comparison of the calculated and experimental values shows that the role of polarisation interaction is considerable in comparatively weakly bonded complexes, the contribution of electrostatic forces being comparable to the contribution of charge-transfer forces. In stronger complexes, the charge-transfer forces predominate over the classical intermolecular interaction forces.

A similar situation probably obtains also for hydrogen-bonded complexes. The hypothesis of a large contribution of charge-transfer forces to the stabilisation energy of hydrogen bonds and of the possibility of considering hydrogen-bonded complexes from the common standpoints of the donor–acceptor interaction and of Mulliken's theory of charge-transfer complexes[41,42] has been frequently put forward[43–48]. In recent years this concept has been increasingly accepted and confirmed experimentally[47,48].

Whereas Mulliken did not classify hydrogen-bonded complexes as electron-donor-acceptor complexes at the time of the creation of his theory[41], in his later studies it is concluded that these two types of interaction are similar and that hydrogen-bonded complexes can be included in the general classification of charge-transfer complexes[42]. The classification is based on the type of interacting orbitals—the highest occupied molecular orbital of the electron donor and the lowest vacant orbital of the acceptor. From this standpoint, compounds of the type A–X–H can be regarded as σ acceptors; charge is transferred from the electron donor to the antibonding orbital of the X–Hσ bond. Hence it follows that the complexes A–H...B can be logically regarded as part of the series of other EDA complexes.

The main success of Mulliken's theory is that it explained the appearance in the electronic spectrum after complex formation of a new absorption band, the so called charge-transfer band. The fact that charge-transfer bands have not so far been reliably observed in the spectra of hydrogen-bonded complexes to some extent inhibits the extension of this theory to such complexes[11,12]. Nevertheless, the spectra of the most stable EDA complexes of Group III metals with different n donors also failed to exhibit charge-transfer bands. Calculations have shown[49,50] that these bands should occur in the region of ultraviolet spectrum which is difficult to investigate experimentally (below 200 nm). Some investigators[46,47,51] suggest with justification that the charge-transfer bands for hydrogen-bonded complexes also occur in the far ultraviolet.

The observed discrepancy between the enthalpies of formation or stability constants of the complexes of a given acceptor A–H with a series of donors B and the ionisation potentials on the latter is sometimes quoted as evidence against the possibility of treating hydrogen-bonded complexes as charge-transfer complexes[11]. It is noteworthy that such a discrepancy is frequently observed also for typical EDA complexes[28]. Although the ionisation potential is an important characteristic of the donor molecule, it is not the only quantity which determines the relative stabilities of the complexes. The conditions governing the overlapping of the interacting donor and acceptor molecule orbitals are very important in the formation of an intermolecular bond. This can be seen, for example, from a comparison of the corresponding parameters of the hydrogen-bonded complexes and iodine complexes. The ionisation potentials I (eV) of the analogous amines, phosphines, sulphides, and ethers, the overlap integrals S between the orbital of the corresponding heteroatom (indicated in brackets) and the 5p orbital of iodine or the 1s orbital of the hydrogen atom, and the enthalpies of formation ΔH (kcal mole^{-1}) of the corresponding complexes of iodine (I_2) and p-chloro-phenol (OH) are listed below:

	$(C_2H_5)_3N$	$(C_2H_5)_3P$	$(C_2H_5)_2S$	$(C_2H_5)_2O$
I[52]	7.58	7.86	8.43	9.55
S (I_2)[28]	0.29 ($2sp^3$)	—	0.23 ($3p$)	0.14 ($2sp^2$)
$-\Delta H$ (I_2)[28]	11.4	—	8.5	4.2
S (O—H)[28]	0.48 ($2sp^3$)	0.37	0.36 ($3p$)	0.43 ($2sp^2$)
$-\Delta H$ (O—H)[53,54]	9.9	8.0*	5.0	6.3

* Data for $(C_4H_9)_3P$.

The overlap integrals of the orbitals involved in the formation of the intermolecular bonds in iodine complexes decrease in the sequence amine > sulphide > ether. The ionisation potentials of these compounds increase in the same sequence. Consequently both parameters, the ionisation potential of the donor and the overlap integral of the interacting orbitals, are responsible for the observed sequence of decreasing enthalpies of formation of the corresponding iodine complexes: amines > sulphides > ethers. Similar relations between I, S, and ΔH have been observed also for hydrogen-bonded complexes in the amine–phosphine–sulphide series. Differences have been observed in oxygen compounds. The ionisation potentials of ethers are much higher than those of sulphides and yet the former give rise to much more stable complexes. This discrepancy can be accounted for by the more effective conditions for the overlapping of the interacting orbitals in the O–H...O (S = 0.42–0.43) linkages[28] than in the O–H...O (S = 0.36)[28] linkages.

From the theoretical standpoint, the increment in the dipole moment $\Delta\mu$ on complex formation is the most interesting property of donor–acceptor complexes. In terms of the approximation of the vector additivity method, $\Delta\mu$ is determined as the vector difference between the dipole moment of the complex μ_c and the dipole moments of the components μ_{A-H} and μ_B. $\Delta\mu$ is directly related to the

charge transferred from the electron donor molecule to the electron acceptor molecule. The determination of the nature of the relation between the magnitude of the transferred charge and the energy of the donor–acceptor bond is of fundamental importance. Comparison of the theoretical and experimental relations may serve as a criterion of the validity of the hypothesis concerning the significant role of charge transfer in the stabilisation of intermolecular bonds.

A linear relation between the degrees of charge transfer and the enthalpies of formation of the complexes has been established on the basis of extensive experimental data embracing a wide variety of complexes of the donor–acceptor type, the enthalpies of formation of which varied from zero to 20 kcal mole^{-1}.[49] The equation of the straight line is

$$-\Delta H = 35.3\,\frac{\Delta\mu}{e\,r_{DA}}, \qquad (1)$$

where ΔH, $\Delta\mu$, and r_{DA} are respectively the heat of formation, the dipole moment increment, and the length of the donor–acceptor bond and e is the electronic charge. A similar linear relation between ΔH and $\Delta\mu$ has been established also for various hydrogen-bonded complexes, the energies of which were between 4 and 26 kcal mole^{-1}.[47,48]

Using the relation between the intensity of the stretching vibration band of A–H in the infrared spectrum of the hydrogen-bonded complex, the energy of formation of the hydrogen bond, and the dipole moment increment on complex formation, Iogansen[57] also concluded that there is a linear relation between ΔH and $\Delta\mu$.

The linear relation between ΔH^0 and $\Delta\mu/er_{DA}$ follows from Mulliken's theory of charge-transfer complexes, which has been described in fair detail in a number of monographs[28,42,58–61]. Here we shall only quote the fundamental equations necessary for the determination of the nature of the relation between the most important parameters of the complexes. According to Mulliken[40,41], the wave function of the ground state of a molecular complex DA can be formulated to a first approximation as the sum of two terms:

$$\psi_N = a\psi_0(\mathrm{D, A}) + b\psi_1(\mathrm{D^+ - A^-}). \qquad (2)$$

The wave function ψ_0 refers to the state of the system without bonding. The interaction between the donor D and the acceptor A takes place via the classical electrostatic forces. The function ψ_1 refers to the state in which the electron has been transferred from the donor to the acceptor. The coefficients a and b characterise the contribution of the structure with charge transfer to the ground state of the complex.

The wave function of the complex in the excited state is

$$\psi_E = a^*\psi_1(\mathrm{D^+ - A^-}) - b^*\psi_0(\mathrm{D, A}). \qquad (3)$$

An approximate solution of the Schrödinger equation yields the following expressions for the energies of the ground and excited states of the complex (E_N and E_E) respectively and for the coefficient ratios b/a and b^*/a^*:

$$E_N = E_0 - \frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}; \qquad (4)$$

$$E_E = E_1 - \frac{(H_{11} - E_1S_{01})^2}{E_1 - E_0}; \qquad (5)$$

$$\frac{b}{a} = -\frac{H_{01} - E_0S_{01}}{E_1 - E_0}; \qquad (6)$$

$$\frac{b^*}{a^*} = -\frac{H_{01} - E_1S_{01}}{E_1 - E_0}, \qquad (7)$$

where

$$E_0 = \int \psi_0 H \psi_0 d\tau;\ H_{01} = \int \psi_0 \hat{H} \psi_1 d\tau;\ E_1 = \int \psi_1 \hat{H} \psi_1 d\tau;\ S_{01} = \int \psi_0\psi_1 d\tau = 2S/(1+S^2)^{1/2}$$

are the overlap integrals of the wave functions ψ_0 and ψ_1 and their expression in terms of the overlap integral S of the corresponding interacting orbitals.

The equation for the energy of the charge-transfer band $h\nu_{ct}$ can be obtained from Eqns. (4) and (5):

$$h\nu_{ct} = E_E - E_N = (E_1 - E_0)\left[1 + \left(\frac{b^*}{a^*}\right)^2 + \left(\frac{b}{a}\right)^2\right]. \qquad (8)$$

The dipole moment increment $\Delta\mu$ due to the charge transfer on formation of the donor–acceptor bond can be expressed as follows according to Mulliken's theory:

$$\Delta\mu = \mu_1(b^2 + abS_{01}), \qquad (9)$$

where μ_1 is the dipole moment of the structure with complete charge transfer. It is assumed that approximately

$$\mu_1 = e\,r_{DA}, \qquad (10)$$

where r_{DA} is the distance over which the charge is transferred. If the degree of charge-transfer is defined as $\Delta\mu/er_{DA}$, then, after substituting Eqn. (10) in Eqn. (9), we obtain

$$\frac{\Delta\mu}{er_{DA}} = b^2 + abS_{01}. \qquad (11)$$

The enthalpy of formation of the complex ΔH can be assumed equal to the difference between the energies of the ground state of the complex and the sum of the energies of the initial components ($E_A + E_D$):

$$\Delta H = E_N - (E_A + E_D). \qquad (12)$$

This quantity may serve as a measure of the energy of the donor–acceptor bond.

Simultaneous solution of Eqns. (4), (6), (8), (11), and (12) yields Eqn. (13), which relates the fundamental parameters of the complex—the enthalpy of formation ΔH, the dipole moment of the donor–acceptor bond $\Delta\mu$, and the energy of the charge-transfer band $h\nu_{ct}$:

$$-\Delta H = \frac{h\nu_{ct}}{A} \cdot \frac{\Delta\mu}{er_{DA}} - [E_0 - (E_A + E_D)], \qquad (13)$$

where

$$A = a^2\left(1 + \frac{a}{b}S_{01}\right) \cdot \left[1 + \left(\frac{b^*}{a^*}\right)^2 + \left(\frac{b}{a}\right)^2\right].$$

For fairly stable complexes, the term $E_0 - (E_A + E_D)$, which is a measure of the energy of the interaction between the donor and acceptor molecules via the classical electrostatic forces, may be regarded as small compared with the first term of Eqn. (13). In this case, Eqn. (13) can be written in the form[28,49,61]

$$-\Delta H^0 = \frac{h\nu_{ct}}{A} \cdot \frac{\Delta\mu}{er_{DA}}. \qquad (14)$$

According to Eqns. (13) or (14), the necessary and sufficient condition for a linear relation between the enthalpy of formation of the complex ΔH^0 and the degree of charge transfer $\Delta\mu/er_{DA}$ is the constancy of the term $h\nu_{ct}/A$ for different complexes. Calculations have shown[49] that, within the limits of the accuracy of the estimates, this quantity is indeed constant and equal to 1–2 eV, in agreement with the coefficient (1.5 eV) in the experimental Eqn. (1).

We may note that the attempts to establish the nature of the correlation between the strength and polarity of

hydrogen bonds have been made frequently. Thus Sutton and coworkers[62,63] compared the dipole moments of hydrogen-bonded complexes with the equilibrium constants K of the complex-formation reactions. However, owing to the linearity of the relation between ΔH and ΔS (as will be demonstrated below), the values of K cannot serve as a sufficiently reliable measure of the energy of the hydrogen bonds. Toyoda[46] attempted to obtain a theoretical description of the relation between ΔH and $\Delta\mu$ on the basis of Mulliken's theory. The following fairly rough approximations were adopted: $a \simeq 1$, $S_{01} = 0$, $\Delta\mu \simeq b^2\mu_1$, $E_0 =$ const., and $H_{01} =$ const.

Assuming that the entropy of complex formation ΔS is constant for different complexes and using the equilibrium constants as a measure of the strength of the hydrogen bonds, Toyoda obtained the relation

$$\lg K \propto \sqrt{\Delta\mu}.$$

However, he correctly remarks in his paper that there are no theoretical grounds for the constancy of H_{01}.

In a recently published series of investigations[64-67], Ratajczak and Orville-Thomas obtained the following expression using the relations from Mulliken's theory and the same approximations as in Toyoda's work:

$$-\Delta H = \frac{H_{01}}{\mu_1^{1/2}}(\Delta\mu)^{1/2} + E_0. \qquad (15)$$

On the basis of Eqn. (15), they concluded that there is a linear relation between ΔH and $(\Delta\mu)^{1/2}$. This correlation was tested using extremely limited experimental data[65].

It must be emphasised that Eqns. (13) and (14), indicating a linear relation between $-\Delta H$ and $\Delta\mu/er_{DA}$, were obtained[49,61] without introducing any approximations additional to those adopted in the derivation of the fundamental equation of Mulliken's theory.

III. HYDROGEN-BONDED COMPLEXES AND PROTON TRANSFER

The hypothesis that the hydrogen-bonded complex is an intermediate in protonation reactions has been gaining increasing recognition at the present time[12]. Proton transfer between the neutral molecules A–H and B via the mechanism

$$\underset{\text{I}}{\text{A—H}} + \text{B} \rightleftarrows \underset{\text{II}}{\text{A—H}\cdots\text{B}} \rightleftarrows \underset{\text{III}}{\text{A}^-\cdots\text{H—B}^+}$$

is believed to be one of the fastest chemical reactions[68].

Not so much the dynamics of the proton transfer process as the question of the positions of the equilibria indicated above is important for the problem discussed in this review. The position of the equilibrium (I) $\rightleftharpoons$ (II) determines in many respects the feasibility and accuracy of the estimation of the parameters of the hydrogen-bonded complexes (see below). The equilibrium (II) $\rightleftharpoons$ (III) determines the state to which the measured parameters refer. The thermodynamic parameters of the formation of hydrogen-bonded complexes are relatively insensitive to the position of the equilibrium (II) $\rightleftharpoons$ (III), since the energetics of the formation of the complex A–H...B and the ion pair A^+...H–B^- in inert solvents are similar[69].

The problem of the origin of the dipole moment of the hydrogen-bonded complex is most controversial. There are two views. According to one, the dipole moment increment on complex formation is caused mainly by the presence in the system of the highly polar protonated form of the complex A^-...H–B^+. The tautomeric equilibrium (II) $\rightleftharpoons$ (III) occurs in solution and the experimental dipole moment includes contributions from the dipole moments of the weakly polar hydrogen-bonded complex and the highly polar ion pair. Hence, $\Delta\mu$ reflects either the tautomeric (II) $\rightleftharpoons$ (III) equilibrium constant[27,70-72] or the mole fraction of species with proton transfer[73-75].

The dipole moment increment is interpreted in a different way from the standpoint of the electron donor-electron acceptor interaction in systems with hydrogen bonds. According to this concept, the differences between the values of $\Delta\mu$ for different hydrogen-bonded complexes are not caused by the different contents of the protonated form of the complex in solution but are determined by the different degrees of charge transfer from the molecule B to the molecule A–H in the hydrogen-bonded complexes. Consequently, the experimental dipole moment refers to the given hydrogen-bonded complex and the dipole moment increment on complex formation is determined to a first approximation by the magnitude of the transferred charge. The ion pair (III) is regarded as the limiting state of the hydrogen-bonded complex.

The non-linearity of the relation between $\Delta\mu$ and ΔpK_a,[27] where ΔpK_a is the difference between the pK_a values of the base and acid, is frequently quoted as one of the pieces of evidence in support of the first view. The S shape of the curves relating $\Delta\mu$ to ΔpK_a is then interpreted from the standpoint of the existence of two forms of the complex, (II) and (III), having different polarities[27,72,74,76]. Furthermore, starting from the investigations of Barrow and coworkers[77,78], who detected by infrared spectroscopy two tautomeric forms of the complex in systems formed by mono- and di-chloroacetic acids with pyridine in chloroform, there have been numerous publications in which the observed changes in the infrared spectra on interaction between acids and bases are treated from the standpoint of the formation of either hydrogen-bonded complexes, or protonated forms of the complex, or of both types of species in equilibrium[79-91]. The latter to some extent justified also the treatment of $\Delta\mu$ from the standpoint of the presence of a tautomeric equilibrium in the system. However, these two types of evidence cannot be regarded as sufficiently reliable.

There exist extensive experimental data showing that the pK_a values cannot serve as a reliable measure of the electron-donating and electron-accepting properties of molecules and of the strength of hydrogen bonds. The nature of these parameters is very complex and they characterise not only the proton affinity of the molecule but include also the energy and entropy of hydration of the components[92]. Arnett et al.[93-95] failed to observe a general correlation between the enthalpies of formation of hydrogen-bonded complexes of a number of bases with *p*-fluorophenol in carbon tetrachloride, on the one hand, and the heats of protonation of these compounds in strong acids (sulphuric and fluorosulphonic), on the other, having shown thereby that the concepts of basicity in these processes are not identical. At the same time, an excellent correlation between the heats of protonation of bases in chlorosulphonic acid and the pK_a values has been demonstrated on the basis of extensive experimental data[95]. The latter is quite natural, since both parameters characterise the formation of solvated ions in the acid–base interaction.

In a study of the interaction of a number of bases with *p*-fluorophenol in carbon tetrachloride and with *p*-fluorobenzenesulphonic acid in methylene chloride by ^{19}F NMR, Taft and coworkers[96,97] showed that the relative basicity scale obtained relative to *p*-fluorophenol (hydrogen-bonded complexes) differs from the basicity scale obtained for

p-fluorobenzenesulphonic acid (ion pairs). As in the previous case, the chemical shifts and ΔH values for the systems with *p*-fluorobenzenesulphonic acid are satisfactorily correlated with the pK_a values measured in water. The dependence of the basicity scales on the acid properties of the proton donor has been demonstrated by Hadzi et al.[98]

In a chromatographic study of the complexes of HCl and HBr with different bases, Iogansen et al.[99] concluded that the capacity for the formation of a hydrogen bond in terms of energy is completely inconsistent with the strength of the acid as defined by the dissociation constant. A similar conclusion, namely that the strength of the hydrogen bond is not determined by the tendency of the proton to pass from the acid to the base (which is measured by the pK_a value), was reached on the basis of the infrared spectroscopic measurements of $\Delta\nu$ and ΔH for the complexes of HX (X = F, Cl, Br, or I) with different bases[100,101]. A similar situation has been observed for compounds containing SH and OH groups. Mercaptans are stronger acids than alcohols, but, other conditions being equal, the compounds RSH form weaker hydrogen-bonded complexes than the analogous compounds ROH.[102]

Thus it is clear from the foregoing that the correlations of particular parameters of hydrogen-bonded complexes with pK_a and ΔpK_a should be treated with much caution. The linearity of the relations between pK_a and some parameter of hydrogen-bonded complexes may be expected only in those cases where the acid–base interaction leads to the formation of solvated ions. The parameters of hydrogen-bonded complexes measured in inert solvents should not be correlated, in principle, with pK_a. This applies, in particular, to the $\Delta\mu$–ΔpK_a correlation, as stated above. The linearity of the relations between ΔH, $\Delta\nu$, and other parameters of hydrogen-bonded complexes, on the one hand, and ΔpK_a, on the other, which is sometimes observed, refers as a rule to a narrow range of similar complexes. The position of the equilibrium (II) $\rightleftharpoons$ (III), which is sometimes observed, depends to a large extent on the medium.

In a study of the complexes of nitrophenols with aliphatic amines in benzene and in a benzene–cyclohexane mixture by ultraviolet spectroscopy, Vinogradov and coworkers[69,103,104] demonstrated the possibility of converting the hydrogen-bonded complex into a protonated form when a relatively small excess of the amine is added to the solutions. The influence of the solvent on the degree of conversion of the hydrogen-bonded complexes into a protonated form has been observed in systems comprising *p*-nitrophenol and various bases in chlorobenzene[105] and in the *p*-nitrophenol–ethylenediamine system in methanol, ethanol, dioxan, and their mixtures with water[106]. Analogous observations concerning the influence of the solvent on the state of the equilibrium (II) $\rightleftharpoons$ (III) were reached also for carboxylic acid–base systems[107-110]. Benzoic acid reacts with triethylamine in inert solvents (cyclohexane, carbon tetrachloride, and carbon disulphide) to form hydrogen-bonded complexes, while in acetonitrile and chloroform ionisation takes place[107]. The conversion of the protonated form of the complex of trifluoroacetic acid with dimethylaniline into a molecular hydrogen-bonded complex has been observed by ^{1}H NMR when the system was diluted with an inert solvent[109].

The results of studies of the infrared spectra of the H_2O–HCl and NH_3–HCl systems in a nitrogen matrix are instructive[111,112]. In an isolated matrix, the complexes H_2O.HCl and NH_3.HCl are not ion pairs but consist of molecular complexes with strong hydrogen bonds. On the other hand, the presence of ionic forms is characteristic of these systems in a number of solvents. The presence of only the molecular complex in solution without an appreciable contribution of the protonated form has been demonstrated by ^{19}F NMR for complexes of *p*-fluorophenol with a wide variety of bases in carbon tetrachloride[113] and other inert solvents[114]. The conclusion that hydrogen-bonded complexes are formed in binary systems of carboxylic acids and phenols with pyridine was reached on the basis of infrared spectroscopic data[115].

Hydrogen-bonded complexes without the formation of the protonated form have been observed also for the hexafluoropropanol–triethylamine[116] and acetic acid–pyridine[117] systems in benzene and for systems comprising HF and different bases[118]. The study of the infrared spectra of the binary and ternary systems formed by a number of carboxylic acids, including strong acids such as trifluoro- and trichloro-acetic acids, with different bases led to the conclusion that only hydrogen-bonded complexes are formed; proton transfer was not observed[119]. The study of the dielectric relaxation times of the complexes formed by picric acid with tributylamine in benzene[120,121] showed that species of only one type exist in solution. The conductivities of the solutions were low.

Thus one can evidently assume with adequate certainty that, in the studies on systems with hydrogen bonds in inert solvents, we are dealing in the vast majority of cases with only one type of hydrogen-bonded complex, namely complex (II), and not with a mixture of the two forms (II) and (III). The measured parameters ($\Delta\mu_c$, ΔH, ΔS, etc.) then refer to the complex A–H...B and are not the overall characteristics of the hydrogen-bonded complex–ion pair equilibrium system.

IV. THE COMPOSITION AND THERMODYNAMICS OF THE FORMATION OF HYDROGEN-BONDED COMPLEXES

We shall now examine the problem of obtaining the most reliable data characterising the properties of the complex A–H...B. Apart from the X–H bond, which behaves as an electron acceptor on formation of the hydrogen-bonded complex, the A–H molecule frequently contains electron-donating atoms or groups. These are oxygen, sulphur, and nitrogen atoms in alcohols, mercaptans, and primary and secondary amines respectively and the CO, PO, and SO groups in carboxylic, phosphoric, and sulphonic acids and the π-electron systems in aromatic and unsaturated compounds. Such polyfunctionality leads in the majority of cases to the self-association of the A–H molecules. The structure of the associated species $(AH)_n$ and the degree of association n depend on the composition and structure of the A–H molecules and on the conditions under which they exist (the state of aggregation, the concentrations in solutions, and temperature)[122-152].

Carboxylic acids tend to form in solution preferentially cyclic dimers[125-132,150]. The association of alcohols and phenols is more complex. Dimers, trimers, and higher polymers, to which both linear and cyclic structures have been attributed, are observed in solutions of these compounds[23,123,133-146]. The problem of the structure of the associated species formed by alcohols and phenols has been extensively discussed in the literature for a long time, but, nevertheless, it still cannot be regarded as finally solved[23,123,138].

The capacity for self association depends both on the electron-donating and the electron-accepting properties of

the A–H molecules. However, in series of compounds A–H with identical structures the introduction of electronegative substituents into the group A leads to a decrease of the capacity of the A–H molecules for self association simultaneously with increase of their electron-accepting capacity. Such a tendency has been observed for alcohols[23], phenols[23,123,139,143], and carboxylic acids[124,128-131]. For example, the enthalpies of formation ΔH_{dim} (kcal mole^{-1}), and the stability constants K_{dim} (litre mole^{-1}) of chloro-substituted acetic acid dimers in carbon tetrachloride decrease with the increase in the number of chlorine atoms in the acid molecule[129]:

	$-\Delta H_{dim}$	K_{dim}
CH_3COOH	8.4	1400
$CH_2ClCOOH$	7.8	701
$CHCl_2COOH$	6.7	600
CCl_3COOH	5.6	150

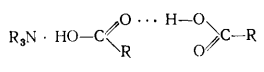
A similar decreased stability of the dimers with increasing degree of halogenation has been observed in a series of substituted fluorophenols[139]:

	$-\Delta H_{dim}$
$2\text{-F}-C_6H_4OH$	5.2
$2,3,5,6\text{-}F_4-C_6HOH$	3.7
C_6F_5OH	2.9

The decreased stability of the associated species leads to a decrease in the tendency of the A–H molecules towards the formation of higher n-mers $(AH)_n$ with $n > 2$. For example, it has been noted that the self-association of polyfluorophenols proceeds via the monomer $\rightleftharpoons$ dimer mechanism, while in solutions of phenols and monofluorophenols, cyclic trimers and tetramers and linear n-mers have been detected[135].

Steric factors also have a significant influence on the capacity of the compounds A–H for self association[132,146]. For example, *ortho*-substituted phenols show less tendency towards self association than their *para*- and *meta*-substituted analogues. The reason for this may be either the formation of intramolecular hydrogen bonds (for example in *o*-nitro and *o*-halogeno-phenols[123,146]) or steric hindrance (for example, the absence of association in 2,6-di-t-butylphenol[146]).

The capacity of the A–H molecules for self-association can lead to the formation, together with the AH...B complexes, also of more complicated complex species having the composition $(AH)_n.B$. The addition of further A–H molecules to AH.B takes place via the same coordination centres as in the self-association of A–H. However, charge transfer from the B molecule to the A–H molecule increases the electron-donating capacity of the latter and the AH...AH linkage is stronger than in the self-associated species[48,53]. For example, the energy of the C=O...H–O hydrogen bond in 2 : 1 complexes of carboxylic acids and amines,



is greater than in the initial acid dimers, the strengthening of this bond being greater the higher the enthalpy of formation of the corresponding complex[48]. The latter is probably associated with the increase of the electron-donating properties of the carbonyl oxygen as a result of charge transfer on formation of the O–H...N linkage.

In view of the self-association of A–H molecules and the possibility of the formation of the complexes $(AH)_n...B$, the interaction in systems with intermolecular hydrogen bonds can be treated as a multistage process:

$$\begin{array}{ll} AH + AH \rightleftharpoons (AH)_2; & AH + B \rightleftharpoons AH \cdot B; \\ (AH)_2 + AH \rightleftharpoons (AH)_3; & AH \cdot B + AH \rightleftharpoons (AH)_2 \cdot B; \\ \cdots\cdots\cdots & \cdots\cdots\cdots \\ (AH)_{n-1} + AH \rightleftharpoons (AH)_n; & (AH)_{n-1} \cdot B + AH \rightleftharpoons (AH)_n \cdot B. \end{array}$$

In solution or in the gas phase, where there is a possibility of the dissociation of the complexes into their components, systems of this kind consist of a complicated equilibrium mixture of complexes having different compositions and of the initial components. In a physicochemical study of such systems, it is necessary to determine simultaneously the parameters of all the complexes present in the mixture, together with their stability constants, which requires the use of special methods for the interpretation of the experimental results[28,153]. If only one comparatively stable complex is formed in the system, the graphical and analytical methods for the interpretation of the measurements[28] used in the study of EDA complexes, which are as a rule approximate, can be applied to the determination of parameters of this complex. For weak interactions or multistage processes, these methods are relatively unsuitable and a rigorous solution of the problem becomes possible only with the aid of a computer[28,53,153].

In order to diminish the degree of self-association of A–H and to avoid the formation of the complexes $(AH)_n.B$, one usually carries out experiments in dilute solutions or a large excess of B is employed. However, the superposition of secondary processes by the appropriate formulation of the experiment is virtually never possible. Thus, if the A–H compounds form fairly stable associated species, self-association can be eliminated only at very low concentrations[53,123] (for example, 0.005M for phenol[123]). Under these conditions, the comparatively weak complexes AH.B can be fully dissociated into their components or can be present in such low amounts that they cannot be detected because of the limited sensitivity of the given physical method. On the other hand, when a large excess of B is used, there is a possibility of complicating effects associated with the solvating action of the medium[53,94].

The experimental results are frequently treated by approximate computational methods, which are suitable only for single-stage complex-formation processes. At the same time, these methods do not involve criteria which would confirm the occurrence in the system of only one postulated equilibrium and do not allow a choice of the concentration conditions in which the superposition of the side process might be neglected[28,53].

The majority of the methods proposed in the literature for the calculation of equilibrium constants and the physical parameters of complexes from physicochemical data obtained in studies on solutions are based on the hypothesis that the solutions are ideal (the activity coefficients of all the components of the complex-formation reaction are unity). However, under real experimental conditions one is not always dealing with ideal solutions[53,94,154-159]. The thermodynamic non-ideality of solutions results, in particular, from the use of solvents with high dielectric constants (nitrobenzene, dichloroethane, etc.) or from the employment of solutions at high concentrations in the experiments. Furthermore, solvents with electron-donating or electron-accepting properties, such as aromatic hydrocarbons, chloroform, methylene chloride, etc. can enter into specific interactions with the components of the test system. The equilibrium constants determined under such conditions are apparent and do not represent the true values[28].

An enormous amount of data has now accumulated on the thermodynamics of the formation of complexes with intermolecular hydrogen bonds. Most of the literature results have been obtained from the temperature variation of the equilibrium constants using a spectroscopic method (ultraviolet, infrared, Raman, and NMR). The standard free energies ΔG^0, enthalpies ΔH^0, and entropies ΔS^0 are determined from the relations

$$\Delta G^0 = -RT\ln K = \Delta H^0 - T\Delta S^0, \quad T = 298\ ^\circ\mathrm{K}; \tag{16}$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \tag{17}$$

ΔH^0 and ΔS^0 are usually found by a graphical procedure based on Eqn. (17) from the slope of the linear plot of $\ln K$ against $1/T$ and from the intercept on the ordinate axis. The possible errors in the determination of K, which were discussed above, can lead to a very significant distortion of the values of ΔH^0, ΔS^0, and ΔG^0 determined from the equilibrium constants[28].

Iogansen and coworkers[57] proposed a spectroscopic method for the determination of the enthalpies of formation of hydrogen-bonded complexes from the intensities of the stretching vibration bands of the groups X–H in the complex and in the free molecule A–H and not on the basis of the equilibrium constants.

It is noteworthy that an additional source of errors in the determination of thermodynamic parameters by spectroscopic methods may be the overlapping of the absorption bands of the initial components and the complexes and also the possible temperature variation of the molar extinction coefficients[8].

Methods for the estimation of the thermodynamic parameters of hydrogen-bonded complexes on the basis of parametric equations have been proposed in a number of studies[6,56,160–163]. For example, Drago et al.[56] proposed a four-parameter equation:

$$-\Delta H^0 = E_D E_A + C_D C_A. \tag{18}$$

The parameters E_D, E_A, C_D, and C_A characterise the electrostatic and covalent properties of the donor and acceptor respectively. The reliability of such parametric methods depends on the accuracy of the estimation of the parameters in the corresponding equations.

The most reliable thermodynamic data for complex-formation reactions can be obtained from direct calorimetric measurements[8,28]. However, here too the accuracy of the determination of the parameters depends to a large extent on the method of mathematical treatment of the results and on the inertness of the medium[28,53]. The Table presents what we believe to be the most reliable thermodynamic parameters (ΔH^0 and ΔS^0) for the complex-formation reactions AH + B ⇌ AH.B. It includes data obtained in the most inert solvents: hexane, cyclohexane, octane, and carbon tetrachloride, and only in a few instances in benzene, toluene, etc. Preference has been given to calorimetric data. Complexes with enthalpies of formation below 4–5 kcal mole^{-1} have been excluded from consideration because the errors associated with the influence of the medium in such cases are comparable to the parameters being determined. Systems where it is virtually impossible to prevent the superposition of side reactions owing to the strong association of the compounds A–H or owing to the presence of additional coordination centres in the donors B are not considered either.

One of the characteristic features of the thermodynamics of the formation of donor–acceptor complexes of

Thermodynamic parameters and dipole moments of hydrogen-bonded complexes.

No.	Complex	$-\Delta H^0$, kcal mole^{-1}	ΔS^0, e.u.	μ_c, D	$\Delta\mu$, D	Solvent	References
1		3	4	5	6	7	8
1	$CH_3OH\cdot N(C_2H_5)_3$	5.4	16.4	2.6	0.55	CH	167
2	$C_4H_9OH\cdot N(C_2H_5)_3$	4.86	14.3	2.51	0.48	CT, CH	195, 66
3	$C_4H_9OH\cdot NC_5H_5$	3.91	11.4	3.37	0.38	CT, B	196, 222
4	$C_6H_{11}OH\cdot NC_5H_5$	3.98	—	4.23	0.8	B	168
5	$CF_3CH_2OH\cdot N(CH_3)_3$	4.8	4.0	—	—	(gas)	197
6	$(CF_3)_2CHOH\cdot OC(CH_3)OC_2H_5$	5.9	13.0	—	—	CT	154
7	$(CF_3)_2CHOH\cdot OC(CH_3)N(CH_3)_2$	8.22	14.7	—	—	H	154
8	$(CF_3)_2OHCH\cdot OP[N(CH_3)_2]_3$	8.63	10.3	—	—	ODCB	154
9	$C_6H_5OH\cdot O(CH_2)_4$	6.06	15.0	3.20	0.69	CT, CH	198, 167
10	$C_6H_5OH\cdot O(CH_2)_4O$	6.0	14.7	1.85	0.39	CT, CH	199, 66
11	$C_6H_5OH\cdot OC(CH_3)_2$	6.6	16.4	5.02	1.04	CH, B	199, 223
12	$C_6H_5OH\cdot OC(CH_3)C_2H_5$	5.34	12.9	4.42	0.51	CT, B	200, 223
13	$C_6H_5OH\cdot OC(CH_3)_5$	5.1	11.4	—	—	CT	201
14	$C_6H_5OH\cdot OC(CH_3)N(CH_3)_2$	7.36	15.0	—	—	CT	202
15	$C_6H_5OH\cdot OS(CH_3)_2$	7.21	13.7	—	—	CT	202
16	$C_6H_5OH\cdot OP(OC_4H_9)_3$	6.1	11.1	—	—	CT	203
17	$C_6H_5OH\cdot OP(SC_4H_9)_3$	5.7	9.9	—	—	CT	203
18	$C_6H_5OH\cdot OP(C_6H_5)_5$	8.1	12.1	—	—	CT	203
19	$C_6H_5OH\cdot OP[N(CH_3)_2]_3$	9.0	15.1	—	—	CT	203
20	$C_6H_5OH\cdot N(C_2H_5)_3$	8.3	19.4	3.01	1.04	CT, CH	204, 66
21	$C_6H_5OH\cdot NC_5H_5$	8.0	18.1	4.30	0.94	CH, HP	199, 66
22	$C_6H_5OH\cdot 2,6\text{-}(CH_3)_2C_5H_3N$	7.8	15.2	—	0.70	CT	205, 74
23	$C_6H_5OH\cdot 2,4,6\text{-}(CH_3)_3C_5H_2N$	7.5	15.7	4.26	0.78	CT	206, 74
24	$4\text{-}CH_3C_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	5.7	10.4	—	—	CT	207
25	$4\text{-}CH_3C_6H_4OH\cdot NC_5H_5$	6.02	13.0	3.84	0.34	CT	196, 74
26	$3\text{-}CH_3C_6H_4OH\cdot NC_5H_5$	6.15	13.4	4.46	1.02	CT, B	196, 168
27	$4\text{-}C_4H_9C_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	8.1	16.0	—	—	CH	208
28	$4\text{-, tert-}C_4H_9C_6H_4OH\cdot O(CH_2)_4$	5.6	12.4	—	—	CH	209
29	$3,4\text{-}(CH_3)_2C_6H_3OH\cdot N(C_2H_5)_3$	7.2	16.6	3.80	1.7	O	53, 47
30	$3,4\text{-}(CH_3)_2C_6H_3OH\cdot NC_5H_5$	7.2	17.0	4.60	1.16	O	53, 47
31	$2,6\text{-}(CH_3)_2C_6H_3OH\cdot N(C_2H_5)_3$	5.4	14.5	3.12	0.95	O, B	53, 47
32	$2,6\text{-}(CH_3)_2C_6H_3OH\cdot NC_5H_5$	6.6	17.2	4.5**	0.95**	O	53, 47
33	$3\text{-}CF_3C_6H_4OH\cdot S(CH_3)_2$	5.4	15.2	—	—	CH	56
34	$3\text{-}CF_3C_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	7.3	11.3	—	—	CH	160
35	$3\text{-}CF_3C_6H_4OH\cdot OC(CH_3)OC_2H_5$	6.8	15.3	—	—	CH	160
36	$3\text{-}CF_3C_6H_4OH\cdot OC(CH_3)_5$	7.4	16.4	—	—	CH	160
37	$3\text{-}CF_3C_6H_4OH\cdot NC_5H_5$	8.5	16.6	—	—	CH	202
38	$4\text{-}FC_6H_4CH\cdot O(C_2H_5)_2$	5.6	14.2	—	—	CT	94, 95
39	$4\text{-}FC_6H_4OH\cdot O(CH_2)_4$	5.7	13.1	—	—	CT	202
40	$4\text{-}FC_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	7.44	13.9	—	—	CT	94, 202
41	$4\text{-}FC_6H_4OH\cdot OS(CH_3)_2$	6.6	10.9	—	—	CT	202
42	$4\text{-}FC_6H_4OH\cdot OS(C_4H_9)_2$	6.3	11.3	—	—	CT	94
43	$4\text{-}FC_6H_4OH\cdot ON(CH_3)_3$	8.8	13.3	—	—	CT	94
44	$4\text{-}FC_6H_4OH\cdot ONC_5H_5$	7.5	12.6	—	—	CT	94
45	$4\text{-}FC_6H_4OH\cdot OP(CH_3)_3$	7.7	10.1	—	—	CT	94
46	$4\text{-}FC_6H_4OH\cdot OP(OC_2H_5)_3$	6.5	9.4	—	—	CT	94
47	$4\text{-}FC_6H_4OH\cdot OP[N(CH_3)_2]_3$	8.0	10.6	—	—	CT	202
48	$4\text{-}FC_6H_4OH\cdot N(C_2H_5)_3$	8.92	21.0	—	—	CT	160, 202
49	$4\text{-}ClC_6H_4OH\cdot O(CH_2)_4$	5.8	12.8	—	—	CT	15
50	$4\text{-}ClC_6H_4OH\cdot OC(CH_3)_2$	4.95	10.3	—	—	CT	210
51	$4\text{-}ClC_6H_4OH\cdot OS(CH_3)_2$	6.7	10.9	—	—	CT	211
52	$4\text{-}ClC_6H_4OH\cdot N(CH_3)_3$	7.4	13.0	4.30	1.4	CH	62
53	$4\text{-}ClC_6H_4OH\cdot N(C_2H_5)_3$	9.9	22.4	4.60	1.75	O	53, 47
54	$4\text{-}ClC_6H_4OH\cdot NC_5H_5$	9.4	20.2	5.07	0.83*	O	53, 47
55	$3\text{-}ClC_6H_4OH\cdot OC(CH_3)_2$	5.3	11.0	—	—	CT	210
56	$3\text{-}ClC_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	6.9	11.7	—	—	CT	211
57	$3\text{-}ClC_6H_4OH\cdot N(C_2H_5)_3$	7.9	20.9	—	—	T	212
58	$4\text{-}BrC_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	7.0	11.7	—	—	CT	207
59	$4\text{-}BrC_6H_4OH\cdot OS(CH_3)_3$	6.8	10.9	5.09	0.71	CT, B	211, 224
60	$4\text{-}BrC_6H_4OH\cdot N(C_2H_5)_3$	10.0	21.7	5.1**	2.24**	O	53, 47
61	$4\text{-}BrC_6H_4OH\cdot NC_5H_5$	8.0	16.3	5.24	0.98	O	53, 47
62	$4\text{-}IC_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	6.5	10.6	—	—	CT	211
63	$4\text{-}IC_6H_4OH\cdot OS(CH_3)_2$	6.6	10.4	—	—	CT	211
64	$4\text{-}CH_3OC_6H_4OH\cdot N(C_2H_5)_3$	8.4	—	2.87	0.61	CT, B	213, 70
65	$4\text{-}CH_3OC_6H_4OH\cdot NC_5H_5$	6.09	13.3	3.69	0.19	CT, B	196, 70
66	$3,4\text{-}Cl_2C_6H_3OH\cdot OC(CH_3)N(CH_3)_2$	7.2	12.6	—	—	CT	211
67	$3,4\text{-}Cl_2C_6H_3OH\cdot OS(CH_3)_2$	7.4	11.8	—	—	CT	211
68	$3,4\text{-}Cl_2C_6H_3OH\cdot N(C_2H_5)_3$	8.0	19.5	—	—	CT	212
69	$4\text{-}NO_2C_6H_4OH\cdot OC(CH_3)N(CH_3)_2$	8.2	11.8	—	—	CT	207
70	$4\text{-}NO_2C_6H_4OH\cdot N(C_2H_5)_3$	9.7	28.6	7.55	2.68	B	47
71	$4\text{-}NO_2C_6H_4OH\cdot N(C_4H_9)_3$	9.3	19.6	—	—	ODCB	214
72	$4\text{-}NO_2C_6H_4OH\cdot NC_5H_5$	8.4	16.4	7.31	0.96	ODCB	214, 74
73	$3\text{-}NO_2C_6H_4OH\cdot N(C_2H_5)_3$	8.5	21.7	5.32	1.20	T, B	212, 70–72
74	$3,4\text{-}(NO_2)_2C_6H_3OH\cdot N(C_2H_5)_3$	8.1	11.1	—	—	B	69
75	$3,4\text{-}(NO_2)_2C_6H_3OH\cdot N(C_8H_{17})_3$	9.2	17.7	—	—	B	69
76	$3,4\text{-}(NO_2)_2C_6H_3OH\cdot N(C_4H_9)_3$	11.0	18.7	—	—	CH	69
77	$C_6H_5COOH\cdot OS(CH_3)_2$	8.8	20.7	—	—	CT	215, 216
78	$C_6H_5COOH\cdot N(C_2H_5)_3$	15.0**	41.3	4.43	3.9	B	48
79	$C_6H_5COOH\cdot N(C_3H_7)_3$	12.9	26.2	4.28	3.8	B	48
80	$CH_3COOH\cdot N(C_2H_5)_3$	11.6	—	3.61	3.5	B	48
81	$CH_3COOH\cdot N(C_3H_7)_3$	11.9	26.5	—	—	B	—
82	$CH_3COOH\cdot N(C_4H_9)_3$	10.0**	19.1	3.80	3.7	B	48
83	$CH_3COOH\cdot NC_5H_5$	7.0	14.5	3.73	2.1	CT, B	217, 225
84	$\text{iso-}C_3H_7COOH\cdot OP(CH_3)_3$	12.0	23.4	—	—	CT	218
85	$CH_2ClCOOH\cdot OS(CH_3)_2$	8.65	11.8	—	—	CT	219
86	$CH_2ClCOOH\cdot OS(C_6H_5)_2$	6.5	7.21	—	—	CT	219
87	$CH_2ClCOOH\cdot OS(CH_2C_6H_5)_2$	7.72	9.39	—	—	CT	219
88	$CH_2ClCOOH\cdot OSe(C_6H_5)_2$	11.8	19.3	—	—	CT	219
89	$CH_2ClCOOH\cdot OP(C_8H_{17})_3$	13.4	21.2	—	—	CT	219
90	$CH_2ClCOOH\cdot OP(C_6H_5)_3$	10.2	16.6	—	—	CT	219
91	$CH_2ClCOOH\cdot N(C_2H_5)_3$	16.2**	42.9	6.71	5.5**	B	48
92	$CH_2ClCOOH\cdot NC_5H_5$	10.3	—	4.80	2.3**	B	48
93	$CH_2BrCOOH\cdot N(C_2H_5)_3$	16.9	46.6	6.84	4.7	B	48
94	$CH_2ICOOH\cdot N(C_2H_5)_3$	16.6	45.6	6.66	4.7	B	48
95	$CHCl_2COOH\cdot OS(CH_3)_2$	9.4	12.0	—	—	CT	219
96	$CHCl_2COOH\cdot OS(C_6H_5CH_3)_2$	9.1	11.8	—	—	CT	219
97	$CHCl_2COOH\cdot OS(C_6H_5)_2$	9.9	7.7	—	—	CT	219
98	$CHCl_2COOH\cdot OSe(C_6H_5)_2$	14.2	23.9	—	—	CT	219

Table (Continued)

No.	Complex	$-\Delta H^0$, kcal mole^{-1}	ΔS^0, e.u.	μ_c, D	$\Delta\mu$, D	Solvent	References
1	2	3	4	5	6	7	8
99	$CHCl_2COOH \cdot OP(C_6H_{17})_3$	23.7	54.4	—	—	CT	219
100	$CHCl_2COOH \cdot OP(C_6H_5)_3$	12.2	19.7	—	—	CT	219
101	$CHCl_2COOH \cdot N(C_2H_5)_3$	21.7	54.4	7.28	5.8	B	48
102	$CF_3COOH \cdot O(C_4H_9)_2$	9.2**	20.5	4.25**	2.3	B	48
103	$CF_3COOH \cdot O(CH_3)_2$	11.8**	29.9	4.81	2.48**	B	48
104	$CF_3COOH \cdot OC(CH_3)C_2H_5$	9.5	23.4	5.38	2.30	B	220
105	$CF_3COOH \cdot OS(CH_3)_2$	13.2	24.5	6.39	2.18	B	220
106	$CF_3COOH \cdot SO_2(C_2H_5)_2$	8.3	18.8	6.33	1.62	B	220
107	$CF_3COOH \cdot SO_2(CH_2)_4$	8.0	18.1	—	—	B	220
108	$CF_3COOH \cdot ON(C_3H_7)_3$	28.3	76.5	11.5	7.3	B	220
109	$CF_3COOH \cdot ONC_5H_5$	16.0	32.6	8.24	4.8	B	220
110	$CF_3COOH \cdot OP(C_4H_9)_2CH_3$	15.7	35.2	7.34	3.1	B	220
111	$CF_3COOH \cdot OP(OC_2H_5)_3$	11.2	18.8	5.71	2.6	B	220
112	$CF_3COOH \cdot OP[N(CH_3)_2]_3$	15.5	26.2	—	—	B	220
113	$CF_3COOH \cdot OAs(C_8H_{17})_3$	22.0	49.6	9.49	3.57	B	220
114	$CF_3COOH \cdot N(C_2H_5)_3$	26.0	49.3	7.55	5.7	B	48
115	$CF_3COOH \cdot N(C_3H_7)_3$	25.7	—	8.38	6.5	B	48
116	$CF_3COOH \cdot N(C_4H_9)_3$	26.0	64.4	8.66	6.8	B	48
117	$CF_3COOH \cdot N(CH_3)_2C_6H_{11}$	26.8	69.5	7.38	5.4	B	48
118	$CF_3COOH \cdot NC_5H_5$	18.4	49.7	6.92	3.6	B	48
119	$CCl_3COOH \cdot O(C_4H_9)_2$	9.8	—	4.2**	2.14**		47
120	$CCl_3COOH \cdot O(CH_2)_4$	11.5**	28.7	4.86**	2.43**		47
121	$CCl_3COOH \cdot OS(CH_3)_2$	10.1	12.6	5.62	2.11	CT, B	219, 224
122	$CCl_3COOH \cdot OS(CC_6H_5CH_3)_2$	9.7	11.7	—	—	CT	219
123	$CCl_3COOH \cdot OS(C_6H_5)_2$	7.4	8.0	6.22	2.61	CT, B	219, 224
124	$CCl_3COOH \cdot OSe(C_6H_5)_2$	15.9	28.7	—	—	CT	219
125	$CCl_3COOH \cdot ONC_5H_5$	22.0	60.4	6.93	3.19	B	220, 224
126	$CCl_3COOH \cdot OP(C_8H_{17})_3$	17.3	—	6.47	1.9	CT	220
127	$CCl_3COOH \cdot OP(C_6H_5)_3$	13.9	24.5	7.1	3.15	CT, B	219, 224
128	$CCl_3COOH \cdot OAs(C_8H_{17})_3$	27.8	121.1	10.74	6.3	B	220
129	$CCl_3COOH \cdot N(C_2H_5)_3$	26.3	69.8	7.46	5.4	B	48
130	$CCl_3COOH \cdot N(C_3H_7)_3$	25.5	63.1	8.19	6.1	B	48
131	$CCl_3COOH \cdot N(C_4H_9)_3$	25.4	66.1	8.82	6.7	B	48
132	$CCl_3COOH \cdot N(C_6H_{11})_3$	24.7	—	9.04	7.0	B	48
133	$CCl_3COOH \cdot N(CH_3)_2C_6H_{11}$	25.6	67.4	7.45	5.2	B	48
134	$CCl_3COOH \cdot NC_5H_5$	17.9	46.6	7.57	4.12	B	48, 239
135	$CBr_3COOH \cdot N(C_2H_5)_3$	24.2	60.1	7.56	5.6	B	48
136	$C_4H_4NH \cdot N(C_2H_5)_3$	5.9	8.2	3.15	0.60	CH	56, 221, 166
137	$CF_3COOH \cdot OAs(C_2H_5)_3$	23.4	58.1	9.36	4.4	B	240
138	$CF_3COOH \cdot OAs(C_6H_5)_3$	20.1	45.1	—	—	B	240
139	$CF_3COOH \cdot SAs(C_2H_5)_3$	10.1	18.5	7.0	1.7	B	240
140	$CF_3COOH \cdot SAs(C_2H_5)_2C_6H_5$	8.5	15.7	—	—	B	240
141	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$CH_3C_6H_4$)	9.1	15.4	—	—	B	240
142	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$CH_3OC_6H_4$)	9.5	16.6	—	—	B	240
143	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$C_2H_5C_6H_4$)	9.6	17.0	—	—	B	240
144	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-FC_6H_4)	8.5	15.1	—	—	B	240
145	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-ClC_6H_4)	8.0	13.7	—	—	B	240
146	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-BrC_6H_4)	8.0	13.8	—	—	B	240
147	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$NO_2C_6H_4$)	7.0	12.0	—	—	B	240
148	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$CH_3COOC_6H_4$)	7.0	11.0	—	—	B	240
149	$CF_3COOH \cdot SAs(C_6H_5)_2C_2H_5$	5.4	9.0	—	—	B	240

* Abbreviations: B = benzene, H = hexane, HP = heptane, O = octane, ODCB = *o*-dichlorobenzene, T = toluene, CH = cyclohexane, CT = carbon tetrachloride.
** These data have been refined in relation to those quoted in the relevant literature (more accurate calculations, replacement of benzene by a more inert solvent—octane).

type $n\nu$ and $n\sigma$ is the so called compensation effect, i.e. a linear relation between ΔH^0 and ΔS^0. As shown previously[164], this relation is general for the complex-formation reactions A + B ⇌ A.B and is described by the equation

$$-\Delta H^0 = -0.337\Delta S^0 + 3.1. \quad (19)$$

A linear relation between ΔH^0 and ΔS^0 was also observed in series of hydrogen-bonded complexes having similar compositions[8,154].

The tabulated data, which cover a wide range of various hydrogen-bonded complexes, are illustrated in Fig. 1, in the form of a plot of ΔH^0 against ΔS^0. Evidently these results fit fairly satisfactorily on a single straight line, whose equation, found by the method of least squares, is

$$-\Delta H^0 = -(0.346 \pm 0.013)\Delta S^0 + (2.77 \pm 0.38). \quad (20)$$

The correlation coefficient is $r = 0.970$.

Within the limits of the confidence intervals, the coefficients of Eqn. (20) agree with those of Eqn. (19).

Consequently the values of ΔH^0 and ΔS^0 for hydrogen-bonded complexes obey the relation characteristic of typical EDA complexes, which demonstrates the identity of the mechanisms of the formation of both types of complexes. A theoretical justification of the linearity of the relation between ΔH^0 and ΔS^0 for the formation of donor-acceptor complexes has been obtained[164] and it has been shown that it is caused mainly by the changes in the intramolecular degrees of freedom on complex formation. The entropy of complex formation can be represented by a sum of two terms:

$$\Delta S = \Delta S_{\text{transl + rot}} + \Delta S_{\text{int}}. \quad (21)$$

The first term of Eqn. (21) reflects the change in the degrees of freedom associated with the motion of molecules as rigid bodies and the second reflects the change in the intramolecular degrees of freedom. The contribution of $\Delta S_{\text{transl. + rot.}}$ is always negative, since the binding of two molecules, and in particular A–H and B molecules, in a complex leads to the loss of three translational and three rotational degrees of freedom. This contribution (50–55 e.s.u.) is almost independent of the stability and structure of the complex[164]. The appearance of six new vibrational degrees of freedom, accompanying the formation of the intermolecular bond, makes the dominant contribution to ΔS_{int}. This contribution is always positive and is greater the lower the energy of the donor–acceptor bond[164]. For this reason, the absolute negative entropy of formation of complexes increases with increase of their enthalpy of formation.

The equilibrium constants for the formation of hydrogen-bonded complexes are frequently used as a measure of their relative stability. Such estimates must be treated with caution. The existence of the so called "isoequilibrium temperature" which is equal to the slope of the ΔH^0–ΔS^0 linear plot, follows from the linear relation between the enthalpy ΔH and entropy ΔS.[164,165] At this temperature (346 ± 13°K or 73° ± 13°C), the equilibrium constants for all complexes obeying Eqn. (21) are similar. At temperatures below the isoequilibrium value, the equilibrium constants increase with the enthalpy of formation of the complexes. Above the isoequilibrium temperature, the opposite relation should hold. Hence it follows that only those values of K which have been obtained below the isoequilibrium temperature may be used for the estimation of the relative energies of the hydrogen bonds.

V. THE STRUCTURE OF HYDROGEN-BONDED COMPLEXES AND ESTIMATION OF THE POLARITY OF HYDROGEN BONDS

Extensive experimental data have accumulated on the dipole moments (DM) of molecular hydrogen-bonded complexes. The Debye method, in which the concentration dependence of the dielectric constants and densities or refractive indices of fairly dilute solutions of the test substances is measured in inert solvents, is the commonest method for the determination of dipole moments. The measurement of the dipole moments of complexes by the Debye method makes it necessary to take into account the equilibrium constants[28], which are either determined by an independent procedure or from dielectric constant measurements simultaneously with μ_c, requiring the use of special methods for the interpretation of the results[28,166-170]. The difficulties arising in the measurements of the dipole moments of hydrogen-bonded complexes in solution and the methods for their determination are similar to

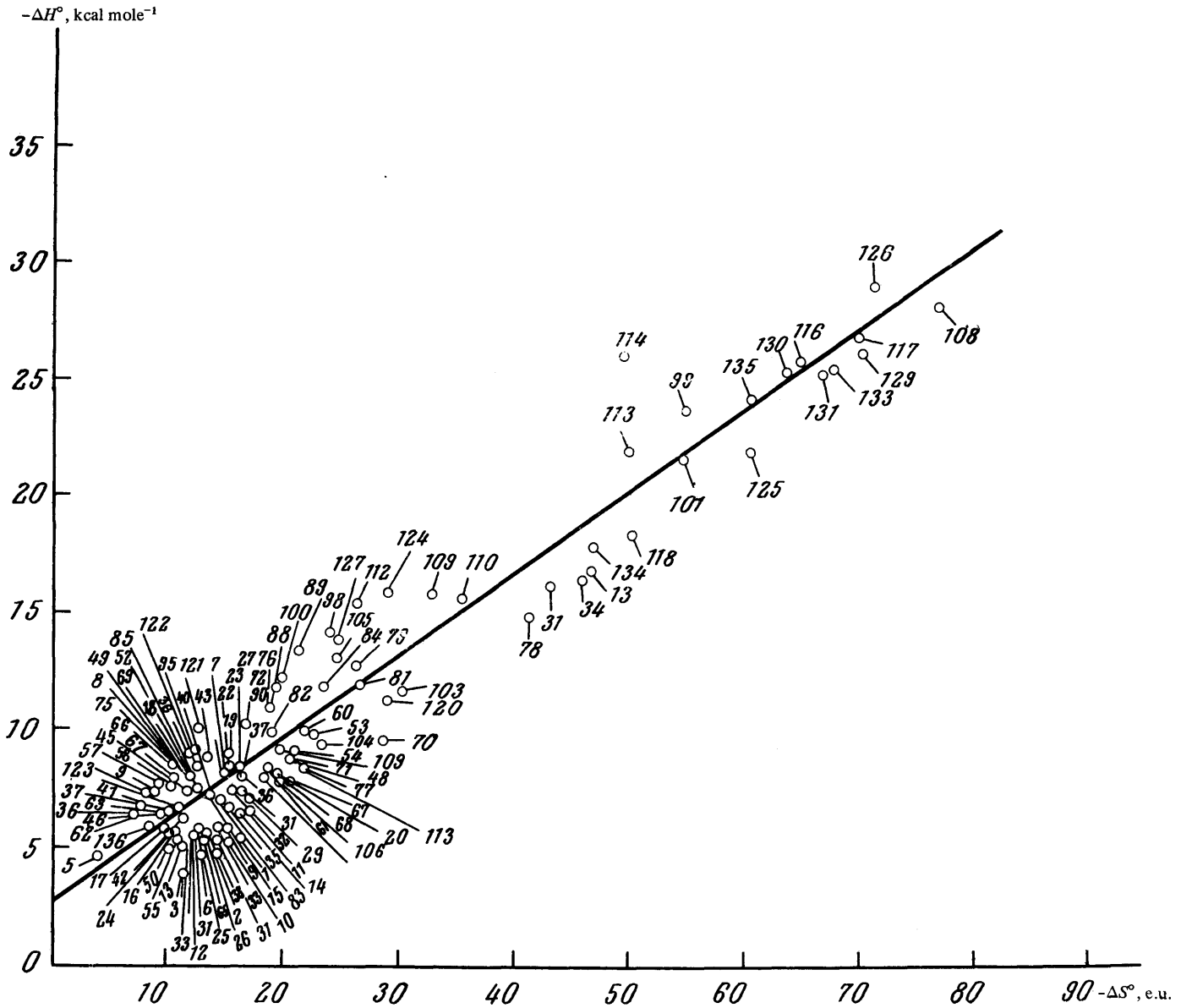


Figure 1. Relation between $-\Delta H^0$ and $-\Delta S^0$ for hydrogen-bonded complexes (the numbers of the points correspond to the numbers in the Table).

those described above for the determination of the thermodynamic parameters. The differences probably consist in the fact that, other conditions being equal, the values of μ_C are less sensitive to the influence of the solvent (naturally, comparatively inert solvents are considered) than the thermodynamic parameters. This is clearly shown, for example, by a comparison of the values of μ_C and ΔH^0 measured by the present authors[47,53] in benzene and octane for the complexes of 4-bromo- and 3,4-dimethyl-phenols with pyridine:

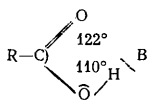
	Benzene		Octane	
4-$BrC_6H_4OH \cdot NC_5H_5$	μ_C	$-\Delta H^0$	μ_K	$-\Delta H^0$
	5.24	6.9	5.30	8.0
3,4-$(CH_3)_2C_6H_3OH \cdot NC_5H_5$	4.40	5.9	4.40	7.2

Within the limits of the present review, we are unable to give a compilation of all the measurements of the dipole moments of hydrogen-bonded complexes. We believe that the Table lists the most reliable dipole moments of such complexes. We may note that, in order to obtain information about the polarity of the intermolecular hydrogen bonds, one mainly considers the simplest systems in which the formation of the intermolecular hydrogen bond is not complicated by an additional interaction. Furthermore, compounds where the enthalpies of formation have been measured as well as their dipole moments are given preference.

Within the framework of the approximation of the vector additivity method for the determination of $\Delta\mu$ (the increment in the dipole moment of a hydrogen-bonded complex

relative to the vector sum of the dipole moments of the components), it is necessary to know not only the values of μ_C, μ_{AH}, and μ_B, but also the angles between these vectors. The available literature data on the structures of hydrogen-bonded complexes are considered below in this connection.

Structure (I) is most probable for the 1 : 1 complexes of carboxylic acids with bases[46,171,172]:

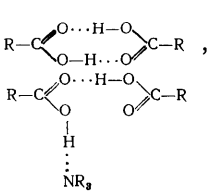


(I)

The planar conformation of the carboxy-group with the *cis*-disposition of the proton of the O–H group relative to C=O has been established by gas-phase electron-diffraction for the formic acid[173] and propionic acid[174] monomers. X-Ray diffraction studies on the 1 : 1 complexes of trichloroacetic acid with pyridine *N*-oxide[172] and of *p*-bromo- and *p*-chloro-benzoic acids with piperidine[175] have shown that the *cis*-conformation of the carboxy-group persists also in the hydrogen-bonded complexes. It was established that complex formation does not cause any significant changes in the structures of the electron donor and electron acceptor molecules, with the exception of the groups directly involved in the formation of the hydrogen bond[175]. This behaviour is characteristic of $n\sigma$ complexes, particularly the complexes of halogens with n donors[28].

The orientation of the B molecules relative to the X–H...Y bond depends on a number of factors. For sterically unhindered compounds, it is determined primarily by the state of the orbital occupied by the free electron pair of the corresponding heteroatom. As in the formation of intermolecular bonds in donor–acceptor complexes, in the hydrogen-bonded complexes the principle of maximum overlap probably holds[28]. From this standpoint, the most probable structure of the complexes of carboxylic acids with amines and phosphines is one where the X–H...Y bond axis coincides with the symmetry axis of the R_3N or R_3P molecule (the sp^3 orbital of the lone electron pair of the heteroatom). In complexes with sulphides and selenides, the planes of the R_2S and R_2Se molecules are almost perpendicular to the X–H...Y axis (p orbital). In complexes with oxygen compounds, the angle between the plane of the donor molecule and the X–H...O axis is approximately 120°, which corresponds to the sp^3 hybridisation of the atomic orbitals of oxygen. However, this angle is not constant in different complexes, appreciable variations being observed[6,28,176].

The problem of the structure of the 2 : 1 complexes of carboxylic acids is still obscure. It has been shown that the hydrogen-bonded ring of the carboxylic acid dimer is planar and has a centre of symmetry[177–184] [structure (II)]. The dissociation of one of the hydrogen bonds in the dimer and the formation of a 3 : 1 complex are associated with significant changes in the conformation of the dimer. Analysis of the dipole moments of such carboxylic acid complexes with amines[48] leads to the conclusion that they most probably have conformation (III):



(II)

(III)

The changes in the structure of phenol molecules on complex formation are insignificant, as for carboxylic acids[192,193]. The orientation of the B molecules relative to the X–H...Y linkages in the complexes of phenols and alcohols was assumed to be the same as in the complexes of carboxylic acids. In the calculations of $\Delta\mu$, the same group dipole moments and valence angles were used as in earlier studies[47,48,171]. The calculated values of $\Delta\mu$ for the corresponding complexes are listed in the sixth column of the Table.

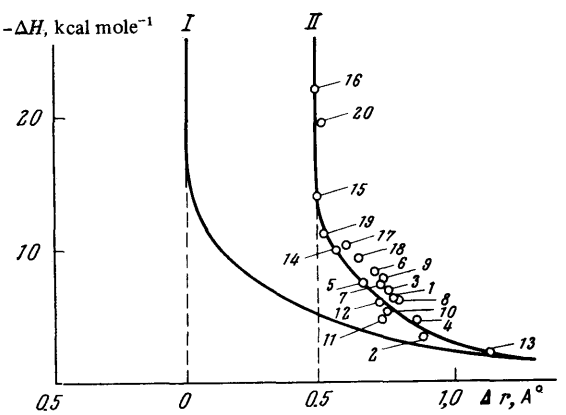


Figure 2. Relation between $-\Delta H^0$ and Δr: I) for typical EDA complexes; II) for hydrogen-bonded complexes; 1) $(CH_3OH)_2$;[226,231] 2) $[2,6\text{-}(CH_3)_2C_6H_3OH]_2$;[143,187] 3) $[3,4\text{-}(CH_3)_2C_6H_3OH]_2$;[142,191] 4) $(4\text{-}ClC_6H_4OH)_2$;[142,191] 5) $(HCOOH)_2$;[184,232] 6) $(CH_3COOH)_2$;[152,233] 7) $[(CH_3)_3.CCOOH]_2$;[184,234] 8) $(C_2H_5COOH)_2$;[151,235] 9) $(C_3H_7COOH)_2$;[184,236] 10) $(CCl_3COOH)_2$;[129,181] 11) $(H_3C\text{-}C{\equiv}C\text{-}COOH)_2$;[126,237] 12) $(C_6H_5COOH)_2$;[149,238] 13) 2,6-$(t\text{-}C_4H_9)C_6H_4.O(CH_2)_4$;[198] 14) $4\text{-}ClC_6H_4OH.N(C_2H_5)_3$;[47,66] 15) $C_6H_5COOH.N(C_2H_5)_3$;[47,66] 16) $C_6H_5COOH.N(C_2H_5)_3$.[232,172]

The energies of the intermolecular hydrogen bonds vary over a wide range: from a few to several tens of kcal mole^{-1} (see the values of ΔH^0 in the Table). Appreciable differences in the X–H...Y bond lengths are observed at the same time. It was of interest to elucidate the relation between these most important parameters of hydrogen-bonded complexes. A relation between ΔH^0 and Δr (Fig. 2, curve I), where $\Delta r = r_{exp} - \Sigma r_{cr}$ is the difference between the experimental length of the donor–acceptor bond and the sum of the covalent radii r_{cr} of the atoms forming this bond, was obtained previously[194] for donor–acceptor complexes of type $n\nu$ and $n\sigma$. For comparatively weak complexes, with enthalpies of formation up to 8–10 kcal mole^{-1}, there is a definite parallelism in the variation of ΔH^0 and Δr: the higher the intermolecular interaction energy the shorter the coordinate bond. The maximum approach of the molecules ($\Delta r = 0$) is reached for $-\Delta H^0 = 14$–16 kcal mole^{-1}. Consequently, when the enthalpy of formation of a particular complex of type $n\nu$ or $n\sigma$ reaches this value, one can assume with a fair degree of certainty that the length of the donor–acceptor bond in this complex is equal to the length of the corresponding covalent bond in conformity with Fig. 2 (curve I).

Naturally, owing to their mutual repulsion, the X, H, and Y atoms in systems with a hydrogen bond cannot form an X–H...Y linkage whose length is equal to the sum of the covalent radii r_X, $2r_H$, and r_Y. However, as in the EDA complexes, here too one may expect a limit to the approach of the molecules for a specific interaction energy. Fig. 2 (curve II) presents a plot of ΔH^0 against Δr for hydrogen-bonded complexes. Here $\Delta r = r_{exp} - \Sigma r_{cr}$, r_{exp} being the experimental X...Y distance in the A–H...B complex and $\Sigma r_{cr} = r_X + 2r_H + r_Y$. In order to plot ΔH^0 against Δr, the most reliable enthalpies of formation and interatomic distances in hydrogen-bonded complexes were used. Owing to the lack of experimental data, the results of quantum-chemical calculations were employed for systems 17–20; for systems 13–15, the bond lengths were obtained from the $\Delta\nu$–r_{XY} correlation[66].

The fact that the nature of the relation between ΔH^0 and Δr for hydrogen-bonded complexes and EDA complexes is the same is most striking. In systems with comparatively weak hydrogen bonds (up to 10 kcal mole^{-1}), the values of Δr increase appreciably with increase of ΔH^0, but for stronger interactions Δr changes little. It is extremely remarkable that the limiting approach of the A–H and B molecules in hydrogen-bonded complexes is reached for approximately the same intermolecular interaction energy as in the usual EDA complexes.

It follows from the analysis of curve (II) in Fig. 2 that Δr is constant and approximately equal to 0.5 Å for complexes with an intermolecular hydrogen bond the enthalpy of formation of which exceeds 12–14 kcal mole^{-1}. Hence one may conclude that, in comparatively stable A–H...B complexes, the minimum X–H...Y distance within the limits of the approximations introduced, may be close to the sum $r_X + 2r_H + r_Y + 0.5$ Å.

The correlation between ΔH^0 and Δr proved extremely useful for the estimation of the intermolecular hydrogen bond lengths $r_{X...Y}$ from the ΔH^0 for the corresponding complexes. We have used it widely for the estimation of the degrees of charge transfer $\Delta\mu/er_{DA}$.

VI. RELATION BETWEEN THE DEGREE OF CHARGE TRANSFER AND THE ENERGY OF HYDROGEN BONDS

The most important evidence in support of the hypothesis that the intermolecular hydrogen bonds are of the donor–acceptor type is provided by the analysis of the relation between the degree of charge transfer and the energy of formation of hydrogen bonds. A linear relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ has been established[47,48] for a number of hydrogen-bonded complexes, mainly those of carboxylic acids and phenols. In the present review, we attempted to survey results referring to a wider range of systems, including the results of studies in recent years.

According to theoretical quantum-chemical calculations, the maximum fraction of the transferred charge is localised near the atom X in the X–H bond. One can assume to a first approximation that the charge is localised at the X atom. In this case, the distance r_{DA} over which the charge has been transferred and which is necessary for the calculation of $\Delta\mu/er_{DA}$ is equal to r_{XY}. We obtained the values of r_{XY} with the aid of a plot of ΔH^0 against Δr (Fig. 2, curve II) using the values of ΔH^0 for the corresponding complexes.

Fig. 3 shows a plot of the relation between the values of $\Delta\mu/er_{DA}$, calculated in terms of the $r_{DA} = r_{XY}$ approximation and the enthalpies of formation of the complexes listed in the Table. Evidently all the results fit fairly satisfactorily on a single straight line. Its equation is found by the method of least squares to be

$$-\Delta H^0 = (38.0 \pm 5.1)\frac{\Delta\mu}{er_{DA}} + (3.9 \pm 1.4). \qquad (22)$$

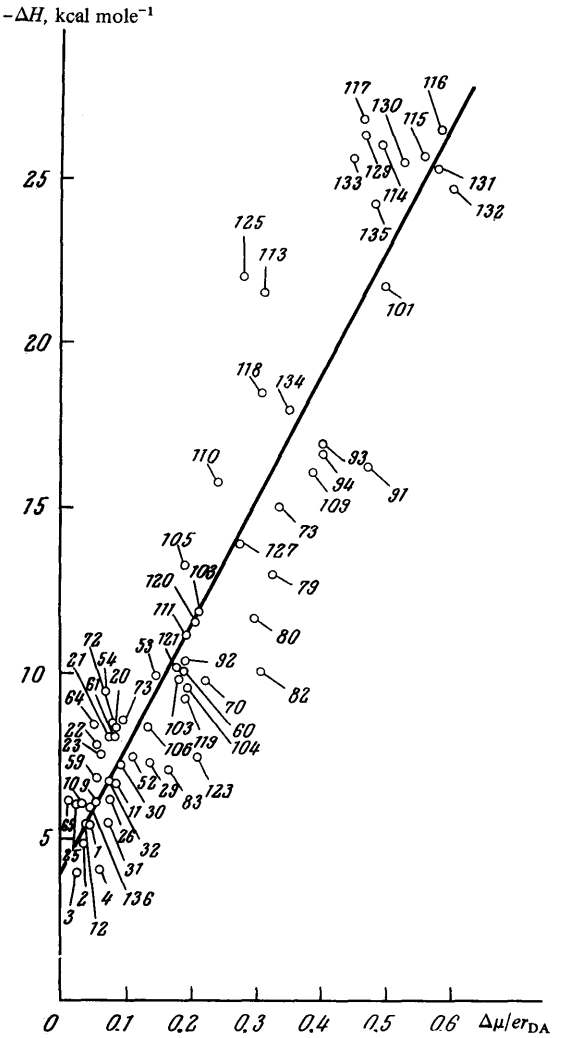


Figure 3. Relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ for hydrogen-bonded complexes (the numbers of the points correspond to the numbers in the Table).

The fairly high correlation coefficient (0.946) shows that, within the limit of the approximations adopted in the calculation of the degrees of charge transfer, one can postulate with a definite degree of certainty a linear relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ for hydrogen-bonded complexes.

The linear correlation between the degree of charge transfer and the energy of intermolecular hydrogen bonds established on the basis of experimental data is consistent

with Eqn. (13) derived from the equations of Mulliken's theory of charge-transfer complexes. According to Eqn. (13), the intercept which the linear plot of $-\Delta H^0$ against $\Delta\mu/er_{DA}$ makes on the ordinate axis is a measure of the energy of the intermolecular interaction via classical electrostatic forces. The value of 3–4 kcal mole^{-1} obtained in Eqn. (22) agrees fully with this hypothesis. The slope of the linear plot of $-\Delta H^0$ against $\Delta\mu/er_{DA}$ is equal, according to Eqn. (13), to the ratio of the energy of the charge-transfer band $h\nu_{ct}$ and the parameter A. The latter can be found from the dipole moment of the complex and the overlap integral for the interacting orbitals[49,61]. According to Eqn. (22), $h\nu_{ct}/A \simeq 1.6$ eV for hydrogen-bonded complexes. On the basis of this quantity and knowing the parameter A for the given complex, it is possible to estimate the position of the charge-transfer band in the electronic spectrum of this complex. The calculations showed that such bands for hydrogen-bonded complexes should occur in the far ultraviolet (below 200 nm).

It is remarkable that the slopes of the linear plots corresponding to Eqns. (1) and (22), which have a fully definite physical significance, agree within their confidence limits. Hence it follows that the relations between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ for hydrogen-bonded complexes and typical EDA complexes are similar. This constitutes an experimental confirmation of the validity of the hypothesis, but there is no fundamental difference between the natures of the forces leading to the formation of both types of complexes.

The linear relation between the degree of charge transfer and the energy of intermolecular hydrogen bonds may be regarded as the most fundamental evidence for the donor–acceptor nature of the hydrogen bond, since this relation actually reflects the main features of the mechanism of the donor–acceptor interaction.

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